hydrous magnesium sulfate and removed to give 0.30 g (65%) acid **48**, and the corresponding methyl ester **49** was prepared with excess diazomethane: IR 1735 (–COOR), 1675 cm^{-1} [c-C(=O)-CH=$CH(CH_2)_3$]; NMR ($CDCl_3$) δ 6.49 (br s, 1 H, vinylic), 3.72 (s, 3 H, –OMe) 1.73 (d, 3 H, J = 2 Hz, CH_3CH=C), 1.13 (s, 3 H, CH_3); UV λ_{max} (MeOH) 236 mm (ϵ 5.5 × 10^3); MS M^+ 224, calcd 224.

Ketalization of 5,6,7,7a-tetrahydro-4,7a-dimethylindan-2(4*H*)-one (50). Ketalization of 0.31 g (1.9 mmol) of **50** was carried out in 70 mL of dry benzene, 2.4 mL of ethylene glycol, and 31 mg of *p*-toluenesulfonic acid for 5 days and worked up as usual. Oil (0.43 g) was obtained in quantitative yield. According to the NMR the ratio **51**/**52** was 7:3. **51**: NMR ($CDCl_3$) δ 3.93 (br, 4 H, J = 3 Hz, –OCH_2CH_2O–), 2.63 (bs, 2 H, O_2CCH_2C=), 1.87 (s, 2 H, O_2CCH_2–), 1.55 (bs, 3 H, CH_3C=C), 1.13 (s, 3 H, CH_3). **52** NMR ($CDCl_3$) δ 5.25 (bd, 1 H, J = 2 Hz, CH=C), 3.95 (s, 4 H, –OCH_2CH_2O–), 2.00 (s, 2 H, CCH_2–), 1.18 (s, 3 H, CH_3C=C), 1.08 (d, 3 H, J = 6 Hz, CH_3C–).

Isomer **51** was isolated from the mixture following the procedure described for **43**.

4-(4-Hydroxypentyl)-4-methyl-2-cyclopenten-1-one (54). Ozonolysis of 1.08 g (5.2 mmol) of a mixture of **51** and **52** in 100 mL of methylene chloride and 20 mL of methanol at −78 °C was performed as described before. The crude diol (0.81 g; 64%) was isolated: IR 3400 (–OH), 1070 cm^{-1} (ketal); NMR ($CDCl_3$) δ 3.9 (s, 4 H, –OCH_2CH_2O–), 1.18 (d, 3 H, J = 6 Hz, CH_3CH 1.03 (s, 3 H, CH_3).

Crude diol **53** (0.18 g) was dissolved in 140 mL of 1:1 tetrahydrofuran/water and 15 g of oxalic acid and refluxed for 3 h. The reaction mixture was worked up as usual and 0.44 g (74%) of **54** as crude oil was isolated: IR 3460 (OH), 1710 cm^{-1} [c-C(=O)CH=$CH(CH_2)_2$]; NMR ($CDCl_3$) δ 7.52, 6.10 (AB, 2 H, J = 6 Hz, vinylic), 1.25 (s, 3 H, CH_3), 1.08 (d, 3 H, CH_3CH).

The corresponding acetate **55** was prepared from 0.33 g of **54** in 5 mL of pyridine and 0.25 mL of acetyl chloride. The keto acetate **54** was purified on basic alumina plates and elated with 3:7 acetone/hexane in 61% yield: IR 1725 ($OCCH_3$), 1700 cm^{-1} [c-C(=O)-CH=$CH(CH_2)_2$]; NMR ($CDCl_3$) δ 7.45, 6.05 (AB, 2 H, J = 6 Hz, vinylic), 2.03 (s, 3 H, CH_3C–); MS M^+ 224, calcd 224.

Registry No.—**2**, 3287-60-3; **3**, 65969-91-7; **4**, 33948-33-3; **5**, 65969-92-8; **6**, 33919-22-1; **7**, 33919-23-2; **8**, 17299-55-7; **9**, 59586-82-2; **10**, 65969-94-0; **11**, 33948-34-4; **12**, 65969-95-1; **13**, 65969-96-2; **14**, 33948-32-2; **15**, 65969-93-9; **17**, 7478-39-9; **18**, 65898-58-0; **19**, 65969-97-3; **20**, 65969-68-8; **21**, 65969-69-9; **22**, 33919-24-3; **23**, 65969-70-2; **24**, 65969-71-3; **25**, 65898-59-1; **26**, 65969-72-4; **27**, 65969-73-5; **29**, 4071-63-0; **30**, 65898-63-7; **31**, 65969-74-6; **32**, 65969-75-7; **33**, 65969-76-8; **34**, 65969-77-9; **35**, 65969-78-0; **36**, 65969-79-1; **37**, 65898-67-1; **38**, 65898-64-8; **39**, 65969-80-4; **40**, 65969-81-5; **42**, 878-55-7; **43**, 65898-65-9; **44**, 65898-56-8; **45**, 65969-82-6; **46**, 65969-83-7; **47**, 65969-84-8; **48**, 65969-85-9; **49**, 65969-86-0; **50**, 65969-87-1; **51**, 65898-60-4; **52**, 65898-52-4; **53**, 65969-88-2; **54**, 65969-89-3; **55**, 65969-90-6.

References and Notes

(1) M. E. Jung, *Tetrahedron,* **32,** 3 (1976).
(2) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.,* **85,** 207 (1963).
(3) S. Yamada and G. Otani, *Tetrahedron Lett.,* 4237 (1969); K. Hiroi and S. Yamada, *Chem. Pharm. Bull.,* **21,** 47 (1973).
(4) (a) S. F. Martin, *J. Org. Chem.,* **41,** 3337 (1976); (b) S. F. Martin, T. S. Chou, and C. W. Payne, *ibid.,* **42,** 2520 (1977).
(5) E. W. Colvin, S. Malchenko, R. A. Raphael, and J. S. Roberts, *J. Chem. Soc., Perkin Trans. 1,* 1989 (1973).
(6) A. J. Birch and J. S. Hill, *J. Chem. Soc. C,* 419 (1966); 125 (1967).
(7) E. Fernholz and H. E. Stavely, Abstracts, 102nd Meeting of the American Chemical Society, Atlantic City, N.J., Sept. 1941, p 39 M.
(8) J. W. De Leeuw, E. R. De Waard, T. Beetz, and H. O. Huisman, *Recl. Trav. Chim. Pays Bas,* **92,** 1047 (1973).
(9) D. Becker, N. C. Brodsky, and J. Kalo, *J. Org. Chem.,* preceding paper in this issue.
(10) J. A. Marshall and M. T. Pike, *Tetrahedron Lett.,* 3107 (1965).
(11) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.,* **33,** 4060 (1968).
(12) A. J. Birch, P. L. Macdonald, and V. H. Powell, *J. Chem. Soc. C,* 1469 (1970).
(13) D. Becker, D.Sc. Thesis, Haifa (1968).
(14) A. S. Narula and S. Dev, *Tetrahedron Lett.,* 1733 (1969).
(15) A. S. Dreiding and A. J. Tomasewski, *J. Am. Chem. Soc.,* **77,** 411 (1955).
(16) W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *J. Am. Chem. Soc.,* **87,** 5148 (1965).
(17) G. Habermehl and A. Haaf, *Chem. Ber.,* **102,** 186 (1969).
(18) W. G. Dauben, J. W. McFarland, and J. B. Rogan, *J. Org. Chem.,* **26,** 297 (1961).
(19) D. Caine and F. N. Tuller, *J. Org. Chem.,* **34,** 222 (1969).
(20) W. S. Johnson, S. Shulman, K. L. Williamson, and R. Pappo, *J. Org. Chem.,* **27,** 2015 (1962).
(21) Y. Hayakawa, H. Nakamura, K. Aoki, M. Suzuki, K. Yamada, and Y. Hirata, *Tetrahedron,* **27,** 5157 (1971).
(22) D. H. R. Barton, A. D. S. Campos-Neves, and A. I. Scott, *J. Chem. Soc.,* 2698 (1957).
(23) J. C. Aumiller and J. A. Whittle, *J. Org. Chem.,* **41,** 2955 (1976).
(24) F. J. McQuillin, *J. Chem. Soc.,* 528 (1955).
(25) Y. Fukuyama and T. Tokoroyama, *Tetrahedron Lett.,* 4869 (1973).
(26) A. Bayless and H. Zimmer, *J. Org. Chem.,* **34,** 3696 (1969).

Selective Reduction of Alkenes and Alkynes by the Reagent Lithium Aluminum Hydride–Transition-Metal Halide

Eugene C. Ashby* and Jiang J. Lin

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received August 15, 1977

The reactions of alkenes and alkynes with $LiAlH_4$ in admixture with first-row transition-metal halides have been studied in detail. When $LiAlH_4$ and $TiCl_3$, VCl_3, $CrCl_3$, $FeCl_2$, $FeCl_3$, $CoCl_2$, or $NiCl_2$ were mixed in equimolar quantities, alkenes were reduced in quantitative yield to the corresponding alkanes. However, when the transition-metal halide was used in catalytic amount, only $CoCl_2$, $NiCl_2$, and $TiCl_3$ were effective in reducing olefins to alkanes in high yield. 1-Methylcyclohexene (a trisubstituted olefin), which is reduced only poorly by hydrozirconation or $LiAlH_4$–$TiCl_3$, was reduced in quantitative yield by $LiAlH_4$–$CoCl_2$ and $LiAlH_4$–$NiCl_2$. The following olefins were reduced to the corresponding alkanes in quantitative yield by one or more transition-metal halides in admixture with $LiAlH_4$: 1-octene, 1-hexene, *cis*-2-hexene, *trans*-2-hexene, styrene, cyclohexene, and 2-ethylhexene. Phenylacetylene was reduced quantitatively to styrene using $LiAlH_4$–$FeCl_2$ or to ethylbenzene when $LiAlH_4$–$NiCl_2$ was used. Diphenylacetylene could be reduced to *cis*-stilbene in the absence of *trans*-stilbene by $LiAlH_4$–$NiCl_2$. 1-Octyne could be reduced to octane in quantitative yield by $LiAlH_4$–$FeCl_2$ or to 1-octene by $LiAlH_4$–$NiCl_2$. Deuterium incorporation studies indicate that the intermediate transition-metal alkyls formed in these reactions are not stable, as only 12–47% deuterium incorporation is observed except when $TiCl_3$ is used as the catalyst.

Application of transition-metal hydrides in organic synthesis has been an area of considerable interest in recent years. Although the ability of transition-metal hydrides to add to olefins to form C–M bonds has been known for some years,[1] the synthetic utility of this reaction is still under development.

Recently, hydrozirconation of alkenes and alkynes has been shown to yield a versatile intermediate for useful synthetic

0022-3263/78/1943-2567$01.00/0

Table I. Reactions of 1-Octene with $LiAlH_4$–Transition-Metal Halides in 1.0:1.0:0.5 Molar Ratio for $LiAlH_4$–Metal Halide–1-Octene[a]

Expt	Metal halide	Registry no.	Reaction time, h	1-Octene recovery, %	Octane,[b] %
1	$TiCl_3$	7705-07-9	1	0	98
2	VCl_3	7718-98-1	1	100	0
			8	0	93
3	$CrCl_3$	10025-73-7	1	0	100
4	$MnCl_2$	7773-01-5	1	71	25
			8	53	40
5	$FeCl_2$	7758-94-3	1	0	98
6	$FeCl_3$	7705-08-0	1	0	98
7	$CoCl_2$	7646-79-9	1	0	100
8	$NiCl_2$	7718-54-9	1	0	100
9	CuI	7681-65-4	8	95	~5
10	$ZnBr_2$	7699-45-8	8	100	0

[a] Reactions were carried out in THF at room temperature. [b] Yield was determined by GLC using an internal standard.

Table II. Reactions of 1-Octene with $LiAlH_4$–Transition-Metal Halides in 1.0:0.10:1.0 Ratio for $LiAlH_4$–Metal Halide–1-Octene[a]

Expt	Metal halide	1-Octene recovery, %	Octane, %
11	VCl_3	64	42
12	$CrCl_3$	80	19
13	$MnCl_2$	100	0
14	$FeCl_2$	95	5
15	$FeCl_3$	95	5
16	$CoCl_2$	0	98
17	$NiCl_2$	5	94
18	$TiCl_3$	0	95

[a] Reactions were carried out in THF at room temperature for 18 h.

Table III. Reactions of 1-Octene with $LiAlH_4$–Transition-Metal Halides in 1.0:1.0:4.0 Ratio for $LiAlH_4$–Metal Halide–1-Octene[a]

Expt	Metal halide	1-Octene recovery, %	Octane, %
19	VCl_3	8	90
20	$CrCl_3$	6	91
21	$FeCl_2$	0	96
22	$FeCl_3$	18	80
23	$CoCl_2$	17	80
24	$NiCl_2$	17	82
25	$TiCl_3$	0	96

[a] Reactions were carried out in THF at room temperature for 18 h.

Table IV. Reactions of 1-Methylcyclohexene with $LiAlH_4$–Transition-Metal Halides[a]

Expt	Metal halide	Molar ratio, $LiAlH_4$–metal halide–substrate	1-Methylcyclohexene recovery, %	Methylcyclohexane, %
26	VCl_3	1:1:2	100	0
27	$CrCl_3$	1:1:2	100	0
28	$MnCl_2$	1:1:2	100	0
29	$FeCl_2$	1:1:2	67	27
30	$FeCl_2$	1:1:0.5	70	30
31	$CoCl_2$	1:0.1:2	98	2
32	$CoCl_2$	1:1:0.5	0	96
33	$CoCl_2$	1:1:1	0	91
34	$NiCl_2$	1:0.1:2	100	0
35	$NiCl_2$	1:1:1	0	94
36	$TiCl_3$	1:0.1:2	100	0
37	$TiCl_3$	1:1:1	94	2

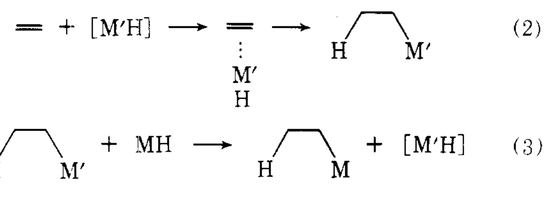
[a] Reactions were carried out in THF at room temperature for 24 h.

transformations.[2] In addition to $Cp_2Zr(H)Cl$, $LiAlH_4$–catalytic $ZrCl_4$[3] has been reported to reduce terminal alkenes to alkanes and $LiAlH_4$–stoichiometric $TiCl_4$[4] was found to be useful for the reduction of alkynes and monosubstituted alkenes. The applicability of these reagents is limited by their low reactivity with higher substituted or strained olefins as well as the need for stoichiometric amounts of the transition-metal reagent. At this stage of development, it would seem important to investigate other transition-metal halides which might be more reactive or generally more attractive than those of zirconium and titanium.

Results and Discussion

Reactions of 1-Octene. The monosubstituted olefin 1-octene was chosen for initial studies of the reaction of olefins with $LiAlH_4$ in the presence of first-row transition-metal halides. The results are shown in Table I. High yields of octane are obtained using $TiCl_3$, $CrCl_3$, $FeCl_2$, $FeCl_3$, $CoCl_2$, and $NiCl_2$ in admixture with $LiAlH_4$. $LiAlH_4$–VCl_3 and $LiAlH_4$–$MnCl_2$ both had lower activities, and $LiAlH_4$–CuI and $LiAlH_4$–$ZnBr_2$ showed no activity at all toward olefin reduction. The transition-metal halide and $LiAlH_4$ were employed in stoichiometric ratio, and the reactive species is presumed to be a transition-metal hydride (eq 1–3). The addition of the transition-metal hydride to the olefin is believed to be due to d orbital overlap between the metal atom and the unsaturated carbon–carbon bond. Under this assumption, Cu(I) (d^{10}) and Zn(II) (d^{10}) have no empty d orbitals to overlap with the olefin and Mn(II) (d^5), with its d orbitals half filled, should exhibit a lower activating ability. This explanation is consistent with the results obtained.

$$MH + M'X \longrightarrow [M'H] + MX \qquad (1)$$



M = Al; M′ = first-row transition metal

In order to investigate the catalytic properties of the first-row transition-metal halides, a 1.0:0.10:1.0 ratio of $LiAlH_4$–metal halide–1-octene was used in experiments 11–18 (Table II). The results show clearly that 1-octene can be reduced to *n*-octane by the combination of $LiAlH_4$ with a catalytic amount of $CoCl_2$, $NiCl_2$, or $TiCl_3$. The same reaction was partially catalyzed by VCl_3 or $CrCl_3$, but little or no catalytic behavior was observed with $MnCl_2$, $FeCl_2$, or $FeCl_3$. It is clear from a comparison of experiments 8 and 17 that the use of catalytic amounts of transition-metal halide ($NiCl_2$ in this case) decreases the rate of reaction. Using a catalytic amount of $NiCl_2$, 5% of 1-octene remains unreacted after an 18-h reaction time, whereas no octene remains after 1 h when a stoichiometric amount of transition-metal halide is used.

Reactions were also carried out using a 1.0:1.0:4.0 ratio of $LiAlH_4$–metal halide–1-octene, and the results are given in Table III.

Table V. Reactions of Other Alkenes with $LiAlH_4$–Transition-Metal Halides

Expt	Metal halide	Alkene[c]	Reaction time, h	Substrate recovery, %	Alkane[c]	Yield of alkane, %
38	$FeCl_2$[a]	Styrene	24	0	Ethylbenzene	95
39	$CoCl_2$[b]			5		92
40	$NiCl_2$[b]			0		92
41	$TiCl_3$[b]			0		94
42	$FeCl_2$[a]	1-Hexene	24	2	Hexane	97
43	$CoCl_2$[b]			0		97
44	$NiCl_2$[b]			0		97
45	$TiCl_3$[b]			0		96
46	$FeCl_2$[a]	*cis*-2-Hexene	24	0	Hexane	98
47	$CoCl_2$[b]			70		32
48	$CoCl_2$[a]			0		98
49	$NiCl_2$[b]			70		28
50	$NiCl_2$[a]			3		95
51	$TiCl_3$			80		18
52	$FeCl_2$[a]	*trans*-2-Hexene	24	0	Hexane	99
53	$CoCl_2$[a]			0		96
54	$NiCl_2$[a]			0		95
55	$TiCl_3$[a]			10		90
56	$FeCl_3$[a]	2-Ethyl-1-hexene	24	20	3-Methylheptane	80
			48	0		95
57	$CoCl_2$[b]		48			35
58	$CoCl_2$[a]		24	0		98
59	$NiCl_2$[b]		48			15
60	$NiCl_2$[a]		24	18		82
			48	0		95
61	$TiCl_3$[b]		48			10
62	$TiCl_3$[a]		24	10		88
			48	2		94
63	$FeCl_2$[a]	Cyclohexene	24	0	Cyclohexane	96
64	$CoCl_2$[b]		48	45		55
65	$CoCl_2$[a]		24	0		96
66	$NiCl_2$[b]		48	60		40
67	$NiCl_2$[a]		24	2		94
68	$TiCl_3$[b]		48	95		0
69	$TiCl_3$[a]		24	60		45
			48	0		95

[a] The molar ratio of $LiAlH_4$–metal halide–olefin is 1.0:1.0:2.0. [b] The molar ratio of $LiAlH_4$–metal halide–olefin is 1.0:0.1:2.0. [c] Registry no.: styrene, 100-42-5; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; 2-ethyl-1-hexene, 1632-16-2; cyclohexene, 110-83-8; ethylbenzene, 100-41-4; hexane, 110-54-3; 3-methylheptane, 589-81-1; cyclohexane, 110-82-7.

Reactions of 1-Methylcyclohexene. The trisubstituted olefin 1-methylcyclohexene was allowed to react with $LiAlH_4$ in admixture with first-row transition-metal halides. The purpose of studying this particular olefin is that it is sterically hindered and does not react by hydrozirconation.[2] Table IV shows that this olefin can be transformed into the saturated hydrocarbon by $LiAlH_4$–$FeCl_2$ (1:1) in 27–30% yield and also reduced by either $LiAlH_4$–$CoCl_2$ (1:1) or $LiAlH_4$–$NiCl_2$ (1:1) in high yields (91–96%). These results with 1-methylcyclohexene reveal that cobalt(II) and nickel(II) salts, when allowed to react with $LiAlH_4$, are better reducing agents than iron(II) or other first-row transition-metal halides in hydrometalation reactions. It is also important to note that this same reaction cannot be carried out catalytically using $CoCl_2$, $NiCl_2$, or $TiCl_3$ or even using a stoichiometric amount of $TiCl_3$.

Reactions of Styrene, 1-Hexene, *cis*-2-Hexene, *trans*-2-Hexene, 2-Ethyl-1-hexene, and Cyclohexene. The monosubstituted olefins styrene and 1-hexene were reduced to ethylbenzene and *n*-hexane in high yield by $LiAlH_4$–equiv/molar ratio of $FeCl_2$ or by catalytic $CoCl_2$, $NiCl_2$, or $TiCl_3$ at room temperature for 24 h (Table V). The disubstituted olefins 2-ethyl-1-hexene, *cis*- and *trans*-2-hexene, and cyclohexene were also reduced by $LiAlH_4$–$FeCl_2$ (1:1 ratio). On the other hand, catalytic amounts of $CoCl_2$, $NiCl_2$, or $TiCl_3$ affected the reduction of the disubstituted olefins at a much slower rate than that of the monosubstituted olefins. However, when stoichiometric amounts of $CoCl_2$, $NiCl_2$, or $TiCl_3$ were used, the rate of reaction accelerated and high yields of products were obtained in 24 h.

Reaction of Phenylacetylene. The terminal alkyne phenylacetylene was allowed to react with $LiAlH_4$–transition-metal halides. When the transition-metal halide was VCl_3, $CrCl_3$, or $MnCl_2$, phenylacetylene was reduced to yield styrene and ethylbenzene without selectivity. Both products appeared from the beginning of the reaction (experiments 70, 72, and 74 in Table VI), showing the competition between alkyne and alkene reduction. In addition, the ratio of $LiAlH_4$–metal halide–substrate seems to be important in suppressing side reactions. For example, the ratio of 1:1:2 exhibited an improved mass balance compared to the ratio of 1:1:3.5. The reaction of $LiAlH_4$–$FeCl_2$ with phenylacetylene was studied carefully (experiments 75–78). The mass balance was increased by decreasing the substrate–reagent ratio as observed in the other transition-metal halide cases. When the ratio is 1:1:2 ($LiAlH_4$–metal halide–substrate), either product can be obtained in high yield. Styrene is obtained by early quenching (10-min reaction time at −40 °C) in 92% yield with no ethylbenzene present. On the other hand, late quenching of the same reaction mixture (24 h at room temperature) produces 85% ethylbenzene in the presence of only 1% styrene. However, 94% ethylbenzene can be obtained when the ratio is 1:1:1 after a 24-h reaction time at room temperature.

Table VI. Reactions of Phenylacetylene with $LiAlH_4$–Transition-Metal Halides

Expt	Metal halide	Molar ratio $LiAlH_4$–metal halide–substrate	Reaction time, h	Phenylacetylene recovery, %	Styrene, %	Ethylbenzene, %
70	VCl_3	1:1:3.5	0.5	92	5	2
			3.0	50	21	13
			24.0	7	40	20
71	VCl_3	1:1:2	1.0	88	11	5
			24.0	0	71	32
72	$CrCl_3$	1:1:3.5	0.5	19	33	27
73	$CrCl_3$	1:1:2	1.0	0	25	62
			24.0	0	7	74
74	$MnCl_2$	1:1:3.5	3.0	53	38	8
			24.0	0	21	53
75	$FeCl_2$	1:1:3.5	0.5	0	37	35
76	$FeCl_2$	1:1:2	1.0	0	14	68
			24.0	0	~1	85
77	$FeCl_2$	1:1:2	10 min[a]	~0	92	~0
78	$FeCl_2$	1:1:1	10 min	0	10	86
			24.0	0	0	94
79	$FeCl_3$	1:1:3.5	0.5	0	37	51
80	$FeCl_3$	1:1:2	1.0	0	10	56
			24.0	0	~1	72
81	$CoCl_2$	1:0.1:3.5	24.0	10	63	13
82	$CoCl_3$	1:0.1:2.0	10 min[a]	55	35	8
			24.0	15	60	21
83	$NiCl_2$	1:0.1:3.5	0.5	0	86	5
			3.0	0	77	16
			24.0	0	62	26
84	$NiCl_2$	1:0.1:2	1.0	0	55	45
85	$NiCl_2$	1:0.1:2	10 min[a]	32	62	0
			30 min[a]	10	88	0
			1.0[a]	0	94	0
			24.0	0	35	65
86	$NiCl_2$	1:0.1:1	10 min	0	45	52
			24.0	0	0	99
87	$TiCl_3$	1:0.1:2	24.0	42	34	5

[a] At −40 °C.

Ferric chloride behaved in a similar fashion to $FeCl_2$, but with a lower mass balance (experiments 77–80). It is also important to note that a catalytic amount of $NiCl_2$ produced the same results as a stoichiometric amount of $FeCl_2$, selectively producing a 94% yield of styrene when the reaction was carried out at −40 °C for 1 h (experiment 85) or ethylbenzene in 99% yield when the reaction was carried out at room temperature for 24 h (experiment 86). The reactions of $LiAlH_4$ with phenylacetylene in the presence of a catalytic amount of $TiCl_3$ or $CoCl_2$ were comparably slower than those employing $NiCl_2$, and they also exhibited inferior selectivities.

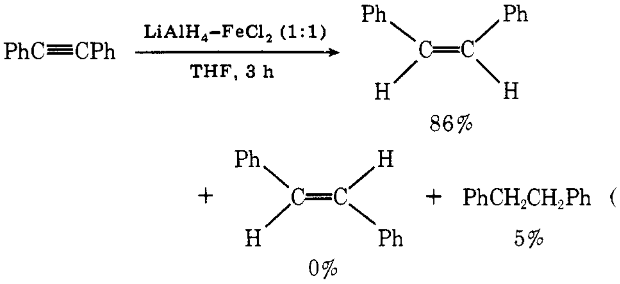
$$PhC{\equiv}CH \xrightarrow[-40\ ^\circ C,\ 10\ min]{LiAlH_4\text{–}FeCl_2\ (1:1)} PhCH{=}CH_2 \quad (92\%) \qquad (4)$$

$$PhC{\equiv}CH \xrightarrow[room\ temp,\ 24\ h]{LiAlH_4\text{–}FeCl_2\ (1:1)} PhCH_2CH_3 \quad (94\%) \qquad (5)$$

$$PhC{\equiv}CH \xrightarrow[-40\ ^\circ C,\ 60\ min]{LiAlH_4\text{–}NiCl_2\ (1:0.1)} PhCH{=}CH_2 \quad (94\%) \qquad (6)$$

$$PhC{\equiv}CH \xrightarrow[room\ temp,\ 24\ h]{LiAlH_4\text{–}NiCl_2\ (1:0.1)} PhCH_2CH_3 \quad (99\%) \qquad (7)$$

Reactions of Diphenylacetylene. Three products are observed in the reaction of $LiAlH_4$–transition-metal halides with diphenylacetylene, i.e., *cis*-stilbene, *trans*-stilbene, and 1,2-diphenylethane (Table VII). Reactions of $LiAlH_4$–VCl_3, –$CrCl_3$, or –$MnCl_2$ with diphenylacetylene are similar to the reactions with phenylacetylene; i.e., no selectivity in product distribution is observed. However, *cis*-stilbene (100% stereoselectivity and 86% yield) was obtained by the reaction of $LiAlH_4$–$FeCl_2$ with diphenylacetylene.



(8)

Both $CoCl_2$ and $NiCl_2$ were also studied by varying the ratio of reagent–substrate, reaction temperature, and reaction time. In general, cis reduction was observed when lower reaction temperatures (−20 or −40 °C) and shorter reaction times were employed. Slight isomerization to the more stable *trans*-stilbene did occur with longer reaction times at room temperature. However, $NiCl_2$ produced 75% *cis*-stilbene with 100% stereoselectivity with only 15% 1,2-diphenylethane after a 24-h reaction time at room temperature. $CoCl_2$ showed less promise as a catalyst, always producing some of the trans olefin or else very low yields of the cis olefin. The reaction using $TiCl_3$ at either room temperature or −40 °C was much slower than the rate of reaction using either $NiCl_2$ or $CoCl_2$.

It is clear from these results that $FeCl_2$ is the best catalyst with $NiCl_2$ the next best in converting alkynes to cis olefins and that cis olefins are the initial products in the reaction. It

Table VII. Reactions of Diphenylacetylene with $LiAlH_4$–Transition-Metal Halides

Expt	Metal halide	Molar ratio, $LiAlH_4$–metal halide-substrate	Reaction time, h	Stilbene, % Cis	Trans	1,2-Diphenylacetylene, %
88	VCl_3	1:1:1	24	26	33	13
89	$CrCl_3$	1:1:1	24	10	47	37
90	$MnCl_2$	1:1:1	24	15	6	2
91	$FeCl_3$	1:1:1	24	17	0	81
92	$FeCl_2$	1:1:1	24	8	8	79
93	$FeCl_2$	1:1:1	1^a	42	0	6
94	$FeCl_2$	1:1:4	1^a	12	0	0
			3	86	0	5
95	$CoCl_2$	1:0.1:1	24	14	14	7
96	$CoCl_2$	1:0.1:1	4^b	24	0	0
			24	18	10	~0
97	$CoCl_2$	1:1:1	1^a	50	Trace	35
98	$CoCl_2$	1:1:4	1^a	52	4	0
			12	72	12	5
99	$NiCl_2$	1:0.1:1	24	13	16	5
100	$NiCl_2$	1:0.1:1	4^b	8	0	0
			24	75	0	15
101	$NiCl_2$	1:1:1	1^a	23	0	52
102	$NiCl_2$	1:1:4	1^b	40	0	0
			12	75	4	5
103	$TiCl_3$	1:0.1:1	24	24	9	18
104	$TiCl_3$	1:1:1	1^a	0	0	0

[a] At −40 °C. [b] At −20 °C.

Table VIII. Reactions of Other Alkynes with $LiAlH_4$–Transition-Metal Chlorides

Expt	Metal halide	Alkyne	Conditions[c]	1-Octene, %	Octane, %
105	$FeCl_2$[a]	1-Octyne	−40 °C, 10 min	80	16
			−40 °C, 1 h	60	37
			RT, 48 h	0	98
106	$CoCl_2$[b]		−40 °C, 1 h	70	17
			RT, 48 h	73	23
107	$NiCl_2$[b]		−40 °C, 1 h	96	1
			RT, 48 h	99	1

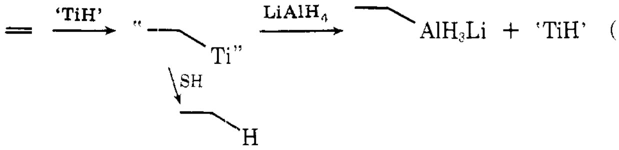
Expt	Metal halide	Alkyne	Conditions[c]	2-Hexene, % Cis	Trans	Hexane, %
108	$FeCl_2$[a]	2-Hexyne	−40 °C, 1 h	55	11	4
			RT, 48 h	16	14	63
109	$CoCl_2$[b]		RT, 2 h	40	5	4
			RT, 48 h	82	4	6
110	$CoCl_2$[a]		−40 °C, 1 h	32	62	0
			RT, 24 h	12	18	62
111	$NiCl_2$[b]		RT, 2 h	40	0	6
			RT, 24 h	91	0	4
112	$NiCl_2$[a]		−40 °C, 1 h	85	0	3
			−40 °C, 2 h	92	0	5
			RT, 24 h	18	20	58

[a,b] See footnotes *a* and *b* in Table V. [c] RT = room temperature.

also appears that with time and higher temperatures the cis olefins isomerize to the trans olefins, which are reduced to the alkanes just like the cis olefins, except at a slower rate. It is also clear from these data that alkynes can be reduced to alkanes directly by using $FeCl_2$ or $FeCl_3$ in admixture with $LiAlH_4$ at room temperature for at least 48 h [for example, 1-octyne is reduced to octane in 98% yield using $FeCl_2$ at room temperature for 48 h (Table VIII)].

Reactions of 1-Octyne and 2-Hexyne. The aliphatic alkynes 1-octyne and 2-hexyne were allowed to react with $LiAlH_4$–$FeCl_2$ (1:1) in THF to produce 1-octene and octane and *cis*- and *trans*-2-hexene and hexane, respectively. The results (Table VIII) show little selectivity on the part of $FeCl_2$ to stop at the octene or *cis*-2-hexene stage. Reactions involving $LiAlH_4$–$CoCl_2$ (1:0.1) showed somewhat better results, but still the reaction is not particularly selective. However, excellent selectivity in reduction was obtained using the reagent $LiAlH_4$–$NiCl_2$ (1:0.1), which reduced 1-octyne to 1-octene in 99% yield with only 0–1% octane formed and reduced 2-hexyne to *cis*-2-hexene in 91% yield with 0% *trans*-2-hexene and 4% hexane formed. It is clear from these results that $LiAlH_4$–$FeCl_2$ is a more powerful agent than $LiAlH_4$–$NiCl_2$ and that both reagents can be used to advantage depending on the ease of reduction of the alkyne or olefin.

Deuterium Incorporation. In order to determine the nature of the reaction intermediate of alkene reduction by $LiAlH_4$ with transition-metal halides, deuterium incorporation experiments were carried out by quenching the reaction mixtures with deuterium oxide. The products were isolated by preparative GLC, and the deuterium content was measured by the molecular ion peak ratio of deuterated–nondeuterated product in the mass spectrum. In reactions involving stoichiometric amounts of $FeCl_2$ or catalytic amounts of $CoCl_2$ or $NiCl_2$, the content of octane-*d* was only 12–26% based on total octane product. The only experiments yielding high amounts of deuterium incorporation involved those reactions with $TiCl_3$ (94% deuterium incorporation). These results imply that the hydrometalation intermediate "—\Ti" is not stable under the conditions studied except in the case of $TiCl_3$. Presumably homolytic dissociation takes place, producing a radical —• which abstracts hydrogen from the solvent (this aspect is being studied further). In other words, the trans metalation reaction from transition-metal alkyl to alkylaluminum intermediate proceeds only in the case of $TiCl_3$ (eq 9).



(9)

Several experiments were attempted to stabilize the carbon–transition-metal bond by varying the ligands attached to the transition metal. It is expected that ligands are capable of stabilizing the transition-metal compounds by dispersing the d orbitals of the transition metal through the attached ligands. A 2-equiv amount of triphenylphosphine was added to $NiCl_2$, which resulted in higher deuterium incorporation (34–42%) and lower rates of reduction. Other nickel halides such as cyclopentadienylnickel chloride and bis(cyclooctadienyl)nickel in the presence of 2 equiv of triphenylphosphine gave 27 and 47% deuterium incorporation, respectively. Although the maximum deuterium incorporation has only reached 47%, the significant improvement compared to $NiCl_2$ shows that the stability of the transition-metal intermediate can be increased by using ligands. We are continuing to study this question.

In conclusion, reactions of $LiAlH_4$–first-row transition-metal halides ($TiCl_3$, VCl_3, $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, CuI, and $ZnBr_2$) with monosubstituted alkenes (1-octene, 1-hexene, and styrene), disubstituted alkenes (2-ethyl-1-hexene, *cis*-2-hexene, *trans*-2-hexene, and cyclohexene), and trisubstituted alkenes (1-methylcyclohexene), as well as terminal alkynes (phenyacetylene and 1-octyne) and internal alkynes (diphenyacetylene and 2-hexyne), have been studied. The ability of alkenes to be reduced by $LiAlH_4$–transition-metal halide reagents was found to be in the following order: Co(II) > Ni(II) > Fe(II) > Fe(III) > Ti(III) > Cr(III) > V(III) > Mn(II) > Cu(I) > Zn(II). Admixtures of $LiAlH_4$–CuI and $LiAlH_4$–$ZnBr_2$ were not effective in alkene reduction. $CoCl_2$, $NiCl_2$, and $TiCl_3$ can catalyze the $LiAlH_4$ reduction of monosubstituted alkenes. VCl_3 and $CrCl_3$ have partial catalytic ability, and no catalytic activity was observed for $MnCl_2$, $FeCl_2$, and $FeCl_3$. Catalysis is slower for disubstituted and trisubstituted alkenes than for the corresponding monosubstituted compounds.

Reduction of alkynes can be carried out quantitatively to give alkenes and alkanes, depending on the transition-metal halide used as a catalyst, the ratio of reagent to substrate, and the reaction conditions. The best reagent is $LiAlH_4$–$NiCl_2$ from the point of view of product selectivity. A cis reduction mechanism is indicated from cis olefin product formation studies.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[5] GLC analyses were performed on F and M Model 720 and 700 gas chromatographs. NMR spectra were obtained on a Varian T-60 spectrometer. Mass spectra were obtained on a Varian Model M-66 mass spectrometer.

Materials. Tetrahydrofuran (Fisher certified reagent grade) was distilled under nitrogen over $NaAlH_4$. $LiAlH_4$ solutions were prepared by stirring $LiAlH_4$ (Alfa Inorganics) in THF overnight followed by filtration through a fritted glass funnel in a drybox.[6] The concentration was determined by aluminum analysis (EDTA). Transition-metal halides [$TiCl_3$, $CrCl_3$, $MnCl_2$, $ZnBr_2$ (Fisher), VCl_3, $FeCl_3$, $CoCl_2$, and $NiCl_2$ (Alfa)] were opened only in a drybox and used without further purification. All organic substrates were purchased commercially and used without further purification. 1-Octene, 1-methylcyclohexene, styrene, *cis*-2-hexene, *trans*-2-hexene, 2-ethyl-1-hexene, cyclohexene, phenylacetylene, diphenylacetylene, 1-octyne, and 2-hexyne were obtained from Chemical Samples Co. or Aldrich.

General Reactions of Alkenes and Alkynes. A 10-mL Erlenmeyer flask with a Teflon-coated magnetic stirring bar was dried in an oven and allowed to cool under nitrogen flush. Transition-metal halide (ca. 3-mmol scale for stoichiometric reaction and ca. 1 mmol for catalytic reaction) was transferred to the flask in a drybox; it was sealed with a rubber septum, removed from the box, and connected by means of a needle to a nitrogen-filled manifold equipped with a mineral oil filled bubbler. A 1–2 mL amount of THF was introduced into the reaction vessel, and then the olefin or alkyne was added. The resulting solution was cooled by means of a dry ice–acetone bath before adding the desired amount of $LiAlH_4$. After 10 min, the reaction was warmed to the desired temperature (−40 °C, −20 °C, or room temp). The reaction was quenched by water, the mixture worked up by extraction with THF, and the resulting solution dried over $MgSO_4$. Most products were separated by GLC using a 6 ft 10% Apiezon L 60–80 S column: 1-octene (110 °C, oven temperature), 1-methylcyclohexene (50 °C), 2-ethyl-1-hexene (50 °C), and cyclohexene (50 °C). A 20 ft 10% TCEP column was used for 1-hexene, *cis*-2-hexene, *trans*-2-hexene, and 2-hexyne (50 °C), and a 10 ft 5% Carbowax 20M column was used for phenylacetylene (90 °C) and diphenylacetylene (200 °C). The yields were calculated by using a suitable hydrocarbon internal standard for each case, and the products were identified by comparing their retention times with those of authentic samples. Yields of *cis*-stilbene [δ 6.60 (vinyl H)], *trans*-stilbene [δ 7.10 (vinyl H)], and 1,2-diphenylacetylene [δ 2.92 (benzyl H)] were determinated by NMR integration and are based on total phenyl protons. However, the ratio of *cis*-stilbene to *trans*-stilbene was also checked by GLC. The yield of adamantane (δ 1.88 and 1.77) was determined by NMR spectroscopy and GLC (Apiezon column). The adamantane was isolated and characterized by its melting point, mp 206–210 °C (lit. 205–210 °C), and mass spectrum, *m/e* 136.5 (M^+) (expected, *m/e* 136.24).

Acknowledgment. We are indebted to the National Science Foundation (Grant No. MPS 7504127) for support of this work.

Registry No.—$LiAlH_4$, 16853-85-3; 1-octene, 111-66-0; octane, 111-65-9; 1-methylcyclohexene, 591-49-1; methylcyclohexane, 108-87-2; phenylacetylene, 536-74-3; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; 1,2-diphenylacetylene, 501-65-5; 1-octyne, 629-05-0; 2-hexyne, 764-35-2.

References and Notes

(1) (a) E. L. Muetterties, *Transition Met. Hydrides 1971*, **1**, Chapter IV (1971); (b) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York and London, 1974, Chapter V.
(2) J. Schwartz, *Angew. Chem., Int. Ed. Engl.*, **15**, 333 (1976).
(3) F. Sato, S. Sato, and M. Sato, *J. Organomet. Chem.*, **122**, C-25 (1976).
(4) P. W. Chum and S. E. Wilson, *Tetrahedron Lett.*, 15 (1976).
(5) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(6) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).